Processes that can be used for the removal of organic precursors (TOC) include enhanced coagulation, granular activated carbon adsorption (GAC), membrane filtration, and chemical oxidation coupled with biofiltration. The only practical process that has been demonstrated to be applicable for the removal of bromide is membrane treatment (i.e. reverse osmosis, and to a lesser extent nanofiltration). The removal of disinfection by-products after they are formed is difficult, primarily because of the wide array of DBPs with their very different physical-chemical properties. An exception is bromate, where several technologies have been examined for its removal. Treatment conditions which can be modified to minimize bromate include decreasing the pH of ozonation to lower the formation of bromate. Disinfectant options include the use of ozone, chloramines, chlorine dioxide, ultraviolet (UV) irradiation, and membrane filtration to partially or fully offset the use of free chlorine.

5.2 Disinfection Practice

The most common chemical disinfectants for the treatment of drinking water are chlorine, ozone and chlorine dioxide. All are capable of inactivating viruses and *Giardia* cysts, at reasonable doses and contact times, in accordance with specifications of the Surface Water Treatment Rule. However, the LT2ESWTR may require greater removal and/or inactivation of Cryptosporidium oocysts. Ozone, and to a lesser extent, chlorine dioxide, appear to be the only chemical disinfectants capable of inactivating Cryptosporidium oocysts, although disinfectant combinations (e.g. free chlorine and chloramines) have been reported to be moderately effective as well. Because of this relationship, the waterworks industry has been moving toward ozonation in place of chlorination for primary disinfection, and many utilities in California that use Delta water have adopted ozonation for primary disinfection and for taste and odor control; ozone is also one of the more effective agents, along with activated carbon, for removing taste and odor-causing organic substances from water. Depending upon criteria developed under the LT2ESWTR, many more utilities may consider ozonation. A major limitation to more widespread practice of ozonation, however, is the fact that ozonation of bromide-containing waters produces bromate. A number of water systems that currently ozonate Delta water experience levels of bromate in excess of the proposed Stage 1 maximum contaminant level for

bromate at certain times of the year, and many are investigating techniques to limit bromate formation or to remove bromate after it is formed.

Other non-chemical or physical options for achieving the *Giardia* and virus removal/inactivation requirements of the Surface Water Treatment Rule and possible Cryptosporidium removal/inactivation requirements include UV-disinfection and membrane filtration. UV-disinfection for cyst inactivation has yet to be demonstrated on a practical, full-scale level, but a number of promising new technologies are under development. The next several years will determine whether or not these new technologies will be practical, and the type of pre-treatment requirements that will be necessary to allow them to function effectively. In contrast, microfiltration has already been demonstrated to be an effective technology for the "absolute" removal of *Giardia* cysts and Cryptosporidium oocysts. Microfiltration will not remove viruses, but tighter membranes, such as nanofiltration or ultrafiltration membranes, can be employed for this purpose. Alternatively, post-treatment of micro-filtered water with free chlorine for only a short contact time can achieve virus inactivation, but in some cases, excessive levels of halogenated disinfection by-products can still be formed, especially in bromide-enriched waters. Two major limitations of membrane filtration processes, particularly nanofiltration and ultrafiltration, are their relatively high costs compared to the more conventional processes, and the fact that they have a product recovery of only about 80% (somewhat greater for ultrafiltration); i.e. a significant amount of the influent water must be wasted, a particularly troublesome limitation for a water-short region like California.

5.3 Removal of Bromide

Bromide occurs as a dissolved species in water and cannot be readily removed by precipitation. It is also not readily removed by coagulation and associated solid-liquid separation processes and tends to pass conservatively through conventional treatment processes. It can be removed by ion exchange, but most resins available today are not very selective for bromide and therefore the process is not very practical for this application. The only processes available at this time for the removal of bromide are reverse osmosis and nanofiltration; bromide rejections of about 90 % and 50 % have been reported, respectively, for these membrane processes. These membrane processes, however, are the most costly of the membrane processes, require the use of

conventional treatment (coagulation, clarification, filtration) prior to their use, and have the lowest recovery, making them relatively impractical for applications in California.

5.4 Removal of Organic Precursors

The most widely studied and demonstrated approach for controlling the formation of disinfection by-products is removal of the organic precursors prior to disinfectant addition. The rationale is that, with lower levels of precursors in the water, the disinfectant demand of the water decreases and lower doses of disinfectants can be applied to achieve the desired level of disinfection, thereby lowering the formation of DBP's. In order of increasing cost and effectiveness, the most viable processes are enhanced coagulation, granular activated carbon adsorption, and membrane filtration. The success of these processes depends significantly upon the nature of the organic material in the water, i.e. whether it is hydrophobic or hydrophilic organic material. Generally, the organic material is characterized in terms of its total organic carbon (TOC) concentration, its ultraviolet (UV) absorbance at 254 nm, or a composite of the two parameters, its specific UV absorbance (SUVA).

Enhanced coagulation involves adding sufficient amounts of coagulant, often more than is typically used for turbidity (particle) removal, to achieve specific TOC removal requirements specified in the proposed Disinfectants/Disinfection By-Products Rule. Given the typical alkalinity and TOC concentration of Delta water, these requirements range from 15 to 40%. SUVA values at exports points are generally in the range of 3 to 4 m^{-1}/(mg C/L). These values indicate that the water likely contains a mixture of non-polar and higher MW versus and polar and lower MW NOM. The water is moderately amenable to coagulation and GAC; membranes would provide the most effective NOM removal. Limitations of practicing enhanced coagulation on Delta water are: the relatively large doses of coagulant required to remove the organic DBP precursors; the corresponding larger amount of sludge that is generated and must be disposed of; the possible need for relatively large amounts of acid to lower the pH in this relatively high alkalinity water to a level where coagulation of organic material is more effective; and the corresponding need for high levels of base to be added to bring the pH back up to acceptable distribution system levels for corrosion control. It should be noted that enhanced coagulation will not remove bromide from the water.

The effectiveness of granular activated carbon (GAC) adsorption for removal of DBP precursors depends upon the empty bed contact time (EBCT) of the carbon bed. Typically, EBCT's in excess of 15-20 minutes are needed for this particular objective. GAC can be used either in a filter-adsorber mode, in which the GAC is added to the conventional filter bed in place of the anthracite and/or sand media, or in a post-filter adsorber, in which a separate GAC adsorption bed is installed. The former approach, because of the relatively low EBCT's in conventional filter beds (5-10 min), is not very effective for precursor removal. Post-filter adsorbers can be designed and operated at any target EBCT, but the cost increases with increasing EBCT. Additionally, the GAC must be regenerated when its adsorptive capacity is reached. The frequency of regeneration ranges from about 3 to 6 months, depending upon the TOC concentration of the water. The cost of GAC increases with increasing frequency of regeneration. GAC will not remove bromide from the water.

A variety of membrane processes are available for water treatment practice, including, in order of increasing relative cost, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The effectiveness of these processes for the removal of organic precursors depends on the size of the pores of the membranes, or more precisely, their molecular weight cutoff (MWCO). MWCO's of 200-500 Daltons are required for effective TOC removal, indicating that NF or RO must be used, although some modest removal can be realized with UF. While microfiltration is effective for the removal of particulate material (e.g. protozoan cysts), it is not fine enough for the removal of TOC, although it can be combined with some powdered activated carbon or coagulant addition to achieve some modest levels of TOC removal. Membrane elements that come in a spiral wound as opposed to a hollow fiber configuration (RO, most NF, some UF) require a substantial degree of pre-treatment to remove particulate material that can cause membrane fouling problems. As noted above, these processes have recoveries on the order of 80% (somewhat higher for NF and UF), making them of dubious practicality for a water-short region like California. Also, as noted above, only reverse osmosis has the ability to reject (remove) bromide.

A number of the larger utilities in California, some of which use Delta water, are currently running bench-scale and pilot-scale studies of GAC adsorption and membrane filtration as part of the EPA's Information Collection Rule to evaluate the effectiveness of these processes for TOC removal and DBP control.

The fact that the majority of these TOC removal processes do not remove bromide means that the bromide/TOC ratio will increase after treatment. As a result, although overall formation of DBPs will be reduced because of the reduced disinfectant requirements, the speciation of the DBPs will shift toward the bromine-containing species such as bromodichloromethane, bromochloroacetic acid, and bromodichloroacetic acid.

One additional treatment approach for removing organic DBP precursors is chemical oxidation and biofiltration. Ozone or advanced oxidation processes involving some combination of ozone, hydrogen peroxide, and UV irradiation, can be employed for this purpose. While these processes do not reduce the TOC concentration appreciably, i.e. they do not convert much of the organic carbon to carbon dioxide, they do alter the nature of the organic material. The oxidation by-products, consisting of aldehydes, organic acids, and other lower molecular weight more oxygenated compounds, are generally more biodegradable than the parent material. Passage of the oxidized water through a biologically acclimatized bed of filter media, e.g. granular activated carbon, anthracite, and/or sand, results in the biological removal of many of these by-products, producing a water with a lower DBP formation potential than the untreated water. Many of the water systems currently using ozone to treat Delta water also employ biological filtration. The effluent from the filters, however, must be treated with a disinfectant such as free chlorine or UV irradiation to inactivate heterotrophic bacteria that are sheared off the filter media. If free chlorine is used for this purpose and the residual precursor concentration in the filter effluent is still significant, appreciable concentrations of DBPs can still be produced, even if the chlorination contact time is relatively short, i.e. on the order of 15 min. This is because the kinetics of DBP formation are more rapid in the presence of bromide. Oxidation coupled with biofiltration is effective only when the water temperature is reasonably warm, e.g. above 10°C. During colder temperatures, the kinetics of microbial degradation are much slower and biofiltration is not as effective. Additionally, if the raw water contains bromide and ozone is the oxidant, bromate formation will occur. Biodegradation of bromate does not occur, except under anoxic conditions which are typically not desirable in water treatment.

5.5. Removal of DBPs

A number of the halogenated organic disinfection by-products produced from chlorination can be removed from the treated water after they have been formed. The trihalomethanes are volatile compounds, i.e. they have low vapor pressures, and can be removed by air stripping. The effectiveness of stripping decreases in the order chloroform, bromodichloromethane, dibromochloromethane, bromoform. These, however, are the only volatile species among the halogenated DBPs and therefore the only ones that can be removed by air stripping. A number of the haloacetic acids have been shown to be biodegradable under aerobic conditions and, accordingly, can be removed by passing, for example, pre-chlorinated water through a biologically active filter bed. The trihalomethanes, however, are biologically stable under aerobic conditions. They can be biodegraded anaerobically, but anoxic treatment is undesirable in water treatment. The haloacetonitriles have been shown to be unstable under elevated pH conditions, undergoing alkaline hydrolysis. Such conditions, however, promote THM formation. The DBP species all have different physical, chemical, and biological properties, hence there is no single treatment process that can be employed to remove them all. Removal of the halogenated organic DBPs after they are formed is therefore not practical; it is a more prudent strategy to try to control their formation by the techniques described above.

Bromate removal, however, may be an effective treatment strategy for controlling bromate levels following its formation by ozonation. Three strategies have been suggested: the use of ferrous iron salts, granular activated carbon adsorption, or UV irradiation. Ferrous iron can chemically reduce bromate to bromide; a ferric hydroxide precipitate is produced that must be removed by subsequent clarification and filtration processes. Hence, such treatment must occur early in the treatment train. pH control is critical to prevent the added ferrous iron from being initially oxidized by dissolved oxygen in the water, although eventual oxidation to ferric hydroxide allows it to function as an iron coagulant. Granular activated carbon can adsorb bromate, but its capacity for doing so is limited, leading to short effective lifetimes for this application of GAC. UV irradiation decomposes BrO_3^- to Br^-, with medium-pressure lamps being more effective than low-pressure lamps. RO and NF membranes can also remove BrO_3^-, but suffer from the same limitation described for Br^- removal. Of these processes, bromate

reduction by ferrous iron appears to be most attractive, but more research and demonstration of this technique needs to be conducted before it can be reliably implemented on a full-scale basis.

5.6 Control of Bromate Formation

A final option for controlling bromate levels in finished drinking water is to minimize its formation in the first place. For example, the extent of bromate formation increases with increasing pH. Hence, pH adjustment to values below 6.5-7.0 prior to ozonation can reduce the formation of bromate. However, as in the case of enhanced coagulation, pH depression requires significant the addition of acid to high-alkalinity waters (Delta water exhibit medium-levels of alkalinity). Additionally, it has been demonstrated that splitting the application of ozone between several of the stages in a multi-stage ozone contactor produces lower levels of bromate than if all of the ozone is applied in the first stage. The judicious use of hydrogen peroxide and ammonia have also been shown to be potentially effective methods for limiting the formation of bromate. Whether or not such modifications can maintain bromate levels below the proposed and potential future MCLs for bromate in waters with elevated bromide levels such as those found in the Delta remains to be demonstrated. Most work to date has focused on the 10 ug/L proposed standard; the efficacy of bromate minimization approaches for a significantly lower MCL has not been studied.

5.7 Matching Treatment to Regulatory Options for Various Source Water Qualities

The national average of Br^- in drinking water sources is significantly less than 100 ug/L. Water exported from the Delta and intended for drinking water has Br^- at levels that are at least the 90th percentile on a national basis. It is noteworthy that BrO_3^- is 63 % Br by weight; this suggests that exceeding the 10 ug/L MCL for BrO_3^- requires only 6.3 ug/L of incorporated Br^-. Br^- is efficiently converted into THM and HAA species, with THM-Br $\approx$ 20 % and HAA_5-Br $\approx$ 10%.

One general approach to examining treatment options to meet various future regulatory objectives is to determine source water quality characteristics in terms of bromide and TOC concentrations that would allow Delta water users to meet these regulations using existing or future water treatment technologies. DBP prediction models; e.g., $BrO_3^- = f(Br^-, etc.)$ or TTHM

= f(Br⁻, etc.); can be used to predict a *limiting* value of Br⁻; e.g., $Br^-_{LIMIT} = f(BrO_3^-{}_{MCL})$ or $Br^-_{LIMIT} = f(TTHM_{MCL})$; to meet a MCL under a given set of water quality (e.g., temperature or pH) and treatment (e.g., O_3 or Cl_2 dose) conditions. Such an exercise was performed by Owen et al. (1998) in assessing potential compliance of Delta water to Stage 1 MCLs for TTHM, HAA$_5$, and BrO_3^- as well as SWTR disinfection requirements by considering coagulation, ozonation, GAC, and membranes. Their conclusion was that TOC and Br⁻ would be contrained to < 3 mg/L and < 50 ug/L, respectively, for utilities incorporating either enhanced coagulation or ozone disinfection; < 5 mg/L and < 50 –100 ug/L for GAC; and < 7 mg/L and < 300 ug/L for (NF) membranes. While Br⁻ and TOC are inter-related, it is Br⁻ that is the limiting factor; since the analysis by Owen et al. (1998) did not consider low-pH ozonation, it would be reasonable to stipulate an upper Br⁻ constraint of 100 ug/L for present SWP treatment practice (conventional treatment with movement toward implementing ozonation and enhanced coagulation). The most flexible treatment approach is membrane treatment, but brine disposal and associated water loss (up to 20 %), as well as cost are serious constraints. It is noteworthy that the models used by Owen et al. (1998) have limitations: the BrO_3^- model used is only applicable to pre-O_3 and the Cl_2 models used do not account for HAA formation nor the reduction in NOM reactivity with treatment.

Krasner (CALFED, 1998) performed bench-scale tests of "synthetic" Delta water (agricultural-drain water diluted with Milli-Q water and spiked with Br⁻) under SDS-chlorination conditions (target Cl_2 residual of 0.5 – 1.5 mg/L, incubation time of 3 hours, pH 8.2, 25°C) and bromate formation potential conditions (O_3/TOC ≈ 2 mg/mg, pH 8.0, 20 °C). These results are summarized in Tables 2 and 3, portraying potential Br⁻ and/or TOC constraints to chlorination and ozonation.

5.8 Summary

Table 4 summarizes the various treatment technologies and their relevance to disinfection and disinfection by-product control in Delta water.

Based on the previous summary, Table 5 matches potential approaches for the treatment of Delta water to meet various possible regulatory options. The approaches may depend

significantly on the bromide, organic carbon content, and the level of fecal contamination in the Delta water.

Table 2. SDS-THM Results Portraying Potential Br⁻ and TOC Constraints.

Br⁻ (ug/L)	TOC (mg/L)				
	1.1	1.4	2.0	3.3	4.2
<10	24	31	38	64	78
100	43	51	60	80	91
200	60	75	83	103	113
400	75	113	128	142	159
800	88	137	182	241	243

Table 3. BrO₃⁻ (ug/L) Formations Results Portraying Potential Br⁻ and TOC Constraints.

Br⁻ (ug/L)	TOC (mg/L)				
	1.2	1.6	2.2	2.9	3.7
<10	<3	<3	4	<3	7
100	6	7	11	12	19
200	11	12	19	25	27
400 - 500	25	23	36	39	49
700 - 900	29	40	53	57	65

Table 4. Matrix of Treatment Processes: Advantages, Disadvantages, Additional Considerations, and Costs.

PROCESS	ADVANTAGES	DISADVANTAGES	ADDITIONAL CONSIDERATIONS	RELA-TIVE COST*
Chlorination	Effective primary disinfectant for *Giardia*, viruses; good secondary disinfectant	Produces halogenated DBPs (THMs, HAAs); ineffective for inactivation of Cryptosporidium	May be effective for Cryptosporidium inactivation when coupled with chloramines	+
Ozonation	Most effective chemical disinfectant for Cryptosporidium; does not produce chlorinated organic DBPs; can be coupled with biofiltration to limit formation of overall organic DBP formation	Produces bromate; can produce brominated organic DBPs; primary disinfectant only; must be coupled with secondary disinfectant such as chlorine or chloramine	Bromate formation can be controlled to some degree by pH adjustment, method of ozone addition; bromate removal possible but requires study	++
Chloramination	Does not produce appreciable THMs or HAAs; good secondary disinfectant for distribution system	Poor primary disinfectant, must be used with free chlorine or ozone as primary disinfectant; does produce unidentified halogenated organic material (TOX) but at lower levels than free chlorine		+
Chlorine Dioxide	Effective primary disinfectant for *Giardia*, viruses; does not produce halogenated DBPs; also inactivates Crypto but not as effectively as ozone	By-product chlorite exhibits acute toxicity; proposed MCL for chlorite of 1.0 mg/L limits use	Chlorite removal may be possible but requires study	+
UV Irradiation	Effective primary disinfectant for viruses; new emerging UV technologies for inactivation of cysts, but not yet demonstrated; does not produce DBPs	Requires use of secondary disinfectant for distribution system	Emerging new UV technologies being evaluated/demonstrated on plant-scale	++